ON THE OXIDATION OF STANNOUS HYDROXIDE IN SODIUM CARBONATE SOLUTION BY MEANS OF AIR.

By **Susumu MIYAMOTO.**

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Introduction. As was described in the previous paper,[1] the oxidation velocity of stannous hydroxide by means of air increases with the increase of the concentration of sodium hydroxide until it attains the dissolution velocity of air into the solution. The increase may be due to the formation of sodium stannite, which dissolves in the solution. The oxidation velocity of stannous hydroxide in sodium carbonate solution can be expected to be very small, as it is almost insoluble in sodium carbonate solution. The present research was carried out to ascertain this idea and as an example of heterogeneous reaction.

Experimental. The experimental procedure was quite the same as that described in the previous paper.[2] In the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal, which is equivalent to the quantity of stannous hydroxide; k was calculated by $k = \frac{1}{t}(v_0 - v)$, v_0 being the value of v at $t = 0$ and $v_{calc.}$ was obtained by $v_{calc.} = v_0 - kt$, using the mean value of k.

TABLE 1.

Temp. = 20° C. Air = 7.78 litres per hour.

$C_{Na_2CO_3}$ normal.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.0155	0	9.52	—	—
	120	8.93	8.80	0.00492
	0	12.23	—	—
	150	11.36	12.33	0.00580
	0	12.84	—	—
	120	12.11	12.12	0.00608
	160	11.98	11.88	0.00538
	0	19.27	—	—
	120	18.43	18.55	0.00700
	160	18.19	18.31	0.00675
	0	19.35	—	—
	150	18.44	18.45	0.00607
				mean: 0.00600

(1) S. Miyamoto, this journal, **2** (1927), 155; *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 189.

(2) Ibid.

TABLE 1. (Continued.)

$C_{Na_2CO_3}$ normal.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.0905	0	10.76	—	—
	120	9.91	9.93	0.00708
	160	9.68	9.66	0.00675
	0	11.52	—	—
	120	10.74	10.69	0.00650
	0	12.23	—	—
	150	11.27	11.19	0.00640
	0	18.00	—	—
	120	17.09	17.13	0.00758
	160	16.87	16.90	0.00706
				mean: 0.00690
0.1655	0	9.43	—	—
	120	8.44	8.51	0.00825
	160	8.21	8.20	0.00763
	0	12.05	—	—
	150	11.01	10.90	0.00693
	0	12.52	—	—
	120	11.61	11.60	0.00758
	160	11.23	11.29	0.00806
	0	17.78	—	—
	120	16.80	16.86	0.00817
	160	16.66	16.55	0.00700
				mean: 0.00766
0.2780	0	11.93	—	—
	120	11.00	11.10	0.00775
	160	10.82	10.82	0.00694
	0	12.31	—	—
	150	11.37	11.27	0.00627
	0	12.87	—	—
	100	12.13	12.18	0.00740
	0	18.14	—	—
	120	17.41	17.31	0.00608
	160	17.02	17.03	0.00700
				mean: 0.00691
0.4655	0	10.02	—	—
	120	9.30	9.19	0.00600
	0	11.52	—	—
	150	10.45	10.49	0.00713
	0	13.19	—	—
	120	12.30	12.36	0.00742
	160	12.04	12.09	0.00719
	0	18.66	—	—
	120	17.78	17.83	0.00733
	160	17.65	17.56	0.00631
				mean: 0.00689

TABLE 1. (Continued.)

$C_{Na_2CO_3}$ normal.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.8405	0	10.51	—	—
	120	9.69	9.72	0.00683
	160	9.50	9.45	0.00631
	0	13.14	—	—
	120	12.46	12.35	0.00567
	0	14.30	—	—
	120	13.50	13.51	0.00667
	160	13.18	13.24	0.00700
	0	19.75	—	—
	120	18.87	18.96	0.00733
	160	18.73	18.69	0.00638
				mean: 0.00660
1.216	0	10.15	—	—
	120	9.40	9.45	0.00625
	160	9.15	9.21	0.00625
	0	13.40	—	—
	120	12.64	12.70	0.00633
	160	12.48	12.46	0.00575
	0	18.32	—	—
	120	17.68	17.62	0.00533
	160	17.49	17.38	0.00519
				mean: 0.00585

As is seen in Table 1, the oxidation velocity of stannous hydroxide is independent of the quantity of stannous hydroxide in sodium carbonate solution approximately, and the effect of the concentration of sodium carbonate on the oxidation velocity is small. The result shows that the oxidation of stannous hydroxide principally takes place in the liquid phase and not on the surface of the solid phase, as in the case of the oxidation of ferrous hydroxide suspended in sodium hydroxide solution by means of air.[1] We see also from the results that stannous hydroxide oxidizes very slowly in the air, and that the rapid increase of the oxidation velocity of stannous hydroxide with the increase of the concentration of sodium hydroxide[2] is due to the formation of sodium stannite which is soluble in the solution.

The Effect of Temperature. The oxidation velocities observed at 30°C. and 40°C. are given in Table 2. The effect of temperature was very small.

(1) S. Miyamoto, this journal, **2** (1927), 40; *Scientific Papers of the Institute of Physical and Chemical Research*; **7** (1927), 35.

(2) S. Miyamoto, this journal, **2** (1927) 158; *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 192.

TABLE 2.

Air = 7.78 litres per hour.

Temp.	$C_{Na_2CO_3}$ normal.	t min.	v c.c.	$v_{calc.}$ c.c.	k
30° C.	0.0155	0	10.26	—	—
		120	9.29	9.37	0.00808
		160	9.11	9.08	0.00719
		0	12.92	—	—
		120	12.09	12.03	0.00692
		160	11.95	11.74	0.00606
		0	19.32	—	—
		120	18.24	18.43	0.00900
		160	18.18	18.14	0.00713
					mean: 0.00740
30° C.	0.0905	0	10.12	—	—
		120	8.97	9.09	0.00958
		160	8.91	8.75	0.00756
		0	13.07	—	—
		120	12.09	12.04	0.00817
		160	11.87	11.70	0.00750
		0	18.88	—	—
		120	17.66	17.85	0.01017
		160	17.55	17.51	0.00831
					mean: 0.00855
40° C.	0.0155	0	9.75	—	—
		90	9.07	9.03	0.00756
		150	8.74	8.55	0.00673
		0	12.19	—	—
		90	11.49	11.47	0.00778
		160	11.05	10.91	0.00713
		0	17.84	—	—
		90	16.96	17.12	0.00978
		150	16.50	16.64	0.00893
					mean: 0.00799
40° C.	0.0905	0	9.81	—	—
		120	8.80	8.78	0.00842
		160	8.59	8.43	0.00763
		0	12.31	—	—
		120	11.27	11.28	0.00867
		160	11.15	10.93	0.00725
		0	18.39	—	—
		120	17.16	17.36	0.01025
		160	16.87	17.01	0.00950
					mean: 0.00862

$\frac{k_{30°}}{k_{20°}} = \frac{0.00740}{0.00600} = 1.23$ $\frac{k_{40°}}{k_{30°}} = \frac{0.00799}{0.00740} = 1.08$, when $C_{Na_2CO_3} = 0.0155$ normal

$\frac{k_{30°}}{k_{20°}} = \frac{0.00855}{0.00690} = 1.24$ $\frac{k_{40°}}{k_{30°}} = \frac{0.00862}{0.00855} = 1.01$, when $C_{Na_2CO_3} = 0.0905$ normal

The oxidation velocity of stannous hydroxide in sodium carbonate solution is thus very small and it was not studied thoroughly. More complete study will be carried out in later occasion.

Summary.

1. The oxidation velocity of stannous hydroxide suspended in sodium carbonate solution of various concentrations by means of air was studied. The oxidation velocity was independent of the quantity of stannous hydroxide.

2. The effect of the concentration of sodium carbonate on the reaction velocity was small.

3. It was ascertained that sodium stannite is oxidized rapidly, while stannous hydroxide is oxidized very slowly by means of air.

4. The effect of temperature on the reaction was small.

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ELECTRICAL CONDUCTANCE OF NICKEL SULPHATE SOLUTION AND IONIC CONDUCTANCE OF NICKEL.

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In the study of the electrode potential of nickel, the results of which will be presented in another paper by the writer, it was necessary to determine the degrees of ionization of its sulphate solutions.

The degree of ionization of a solution is usually expressed by the relation,

$$\alpha = \frac{\lambda}{\lambda_0}\left(\frac{\eta}{\eta_0}\right),$$

where λ is the equivalent conductance of the solution in question, λ_0 that of

an infinitely dilute solution of the electrolyte and η/η_0 is the relative viscosity of the solution which may be taken as unity for sufficiently dilute solutions.

Of these values, the equivalent conductances of nickel sulphate at various concentrations at 25° C. were determined separately by Franke and Jones.[1] However, as these values differ from each other in a not inconsiderable amount, conductivity measurements were made, taking full precaution in preparing the material and in the experiment. Viscosity measurements were also made in parallel.

The equivalent conductance at zero concentration can be calculated by Kohlrausch's principle of additivity from the ionic conductances of the nickel ion and the sulphate ion. Though there are several accurate determinations of the ionic conductance of the latter constituent, Heydweiller's value[2] only is known for the ionic conductance of the former. He has derived this value from the values of equivalent conductance at zero concentration of nickel nitrate, chloride and bromide, which were obtained by the Kohlrausch method of plotting the equivalent conductances at various concentrations against the cube-root of the concentrations. But, his values of λ_0 thus obtained are not reliable, because of the too large extrapolation from the points at some high concentrations to that of the infinite dilution and it is therefore desirable to evaluate λ_0 by some other method of greater accuracy. For this purpose, however, the conductance values of nickel salts, given in Kohlrausch and Holborn's table, are not accurate enough and will lead to giving the value of the ionic conductance of nickel a probable error of more than a few percent.

Therefore, the value of λ_0 of nickel sulphate was obtained by Noyes' method[3] of using Storch's function from the writer's own values of equivalent conductances at various concentrations, which were determined with sufficient accuracy.

Materials. *Conductivity Water.*—The conductivity water was prepared by the usual method of redistilling ordinary distilled water with alkaline permanganate and condensing it by means of a tin condenser. All the water used had a conductivity between 0.7×10^{-6} and 1.0×10^{-6} reciprocal ohm.

Nickel Sulphate Solutions.—Kahlbaum's cobalt-free nickel sulphate was purified by twice recrystallizations from conductivity water. The separate solutions of nickel sulphate were made up by diluting three standardized stock solutions, 1 N, 0.1 N, and 0.02 N, with the conductivity water to the

(1) Kohlrausch and Holborn, "Das Leitvermögen der Electrolyte."
(2) *Z. physik. Chem.*, **89** (1915), 281.
(3) Noyes and Falk, *J. Am. Chem. Soc.*, **34** (1912), 462.

accurate normality desired at 25° C. or 18° C.. The standardization of these stock solutions was made by an electroanalysis for nickel using a rotating anode.[1]

Measurements of Specific Conductances. *Apparatus and Procedure.*—The conductivity was measured by the ordinary Kohlrausch bridge method, using two cells of the Washburn type A and B.[2]

The assembly for the measurement consisted of a Kohlrausch bridge with extension coils, a 5-dial Curtis-coil resistance box (both furnished by the Leeds and Northrup Company), Noguchi's special transformer producing a very audible alternating current suitable for the Kohlrausch bridge,[3] and a tunable telephone. The slide-wire and the resistance box were calibrated just before the conductivity work was began. The cell constants of the conductivity cells were first determined with a 1/10 normal solution of Kahlbaum's best potassium chloride, and were found to have the values of 1.6856 and 0.1754, respectively. Then these cell constants were checked by means of a 1/50 normal solution of potassium chloride.

The specific conductivities of the solutions were measured at 25°±0.02°C. and at 18°±0.02°C. Immediately after the preparation of each solution its conductivity was measured. After filling the conductivity cell, it was placed in the thermostat and left there for about half an hour. The conductance was then measured twice at an interval of fifteen minutes, in order to be assured that the solution had attained the temperature of the bath. Three separate readings with different resistances gave the conductances, which agree within 0.04 %. The cell was then emptied and refilled with the same solution and confirmative measurement was made. The various determinations of the conductance of the same solution using the same resistance agree within less than 0.02 %.

Results.—Table 1 contains the averages of the specific conductances thus obtained at 25° C. and the equivalent conductances calculated from them and Table 2, those at 18° C.

In both tables, the first column gives the concentration in equivalent per liter at the temperature of the measurement; the second, the cell constant; the third, the measured specific conductance in reciprocal ohms, after the correction for instrumental errors (in the slide wire and the resistance coils); and the fourth, the true specific conductance after the water correction, obtained by subtracting the conductance of water from the value of observed specific conductance in the third column. The mean value of the specific conductances of water was 1.02×10^{-6} at 25° C. and

(1) Treadwell-Hall, "Analytical Chemistry" II, p. 136.

(2) *J. Am. Chem. Soc.*, **38** (1916), 2449.

(3) *J. of Inst. of Electrical Engineers of Japan*, (1921) 394; (1923), 421.

0.81×10^{-6} at 18° C. in reciprocal ohm. The last column gives the equivalent conductance calculated from the value of the corrected specific conductance in the fourth column.

TABLE 1.

Conductance of Aqueous Nickel Sulphate Solution at 25° C.

Concentration at 25° C.	Cell constant.	Specific conductance.		Equivalent conductance.
		Observed.	Corrected.	
1	1.6856	29091 $\times 10^{-6}$	29091 $\times 10^{-6}$	29.091
0.5	„	17611 „	17611 „	35.222
0.2	„	8717 „	8717 „	43.585
0.1	„	5075.5 „	5075.5 „	50.755
0.05	„	2958.0 „	2958.0 „	59.160
0.02	0.1754	1446.1 „	1445.1 „	72.254
0.01	„	827.9 „	826.9 „	82.69
0.005	„	466.82 „	465.8 „	93.16
0.002	„	212.00 „	210.98 „	105.49
0.001	„	114.07 „	113.05 „	113.05
0.0005	„	60.35 „	59.331 „	118.66
0.0002	„	25.85 „	24.827 „	124.14
0.0001	„	13.71 „	12.690 „	126.90

TABLE 2.

Conductance of Aqueous Nickel Sulphate Solution at 18° C.

Concentration at 18° C.	Cell constant.	Specific conductance.		Equivalent conductance.
		Observed.	Corrected.	
1	1.6856	25066 $\times 10^{-6}$	25066 $\times 10^{-6}$	25.066
0.5	„	15185 „	15185 „	30.370
0.2	„	7519 „	7519 „	37.595
0.1	„	4383.3 „	4383.3 „	43.833
0.05	„	2550.4 „	2550.4 „	51.008
0.02	0.1754	1241.2 „	1240.4 „	62.02
0.01	„	709.7 „	708.9 „	70.89
0.005	„	398.2 „	397.4 „	79.48
0.002	„	180.68 „	179.87 „	89.94
0.001	„	97.12 „	96.31 „	96.31
0.0005	„	51.31 „	50.50 „	101.00
0.0002	„	21.884 „	21.074 „	105.37
0.0001	„	11.680 „	10.870 „	108.70

Calculation of Equivalent Conductance of Nickel Sulphate at Infinite Dilution and Ionic Conductance of Nickel. The value of λ_0 of nickel sulphate was obtained by employing the graphic method of A.A. Noyes.[1]

The method is as follows: Storch's function $C(\lambda_0-\lambda)=k(C\lambda)^n$, which is equivalent to $\frac{C\alpha}{C(1-\alpha)}=k$, if $\frac{\lambda}{\lambda_0}$ may be taken as a measure of the ionization (α), is transformed into $\frac{1}{\lambda_0}=\frac{1}{\lambda}-k(C\lambda)^{n-1}$, and the values of $(C\lambda)^{n-1}$ in the range from 0.0001 to 0.02 normal are plotted as abscissas against the values of $\frac{1}{\lambda}$ as ordinates, by varying the values of $(n-1)$, until a plot as linear as possible is obtained. The value of λ_0 is obtained graphically by the extrapolation of the plotted line to zero concentration or $C\lambda=0$. In Fig. 1, in order to make the various curves comparable, the value $(C\lambda)^{n-1}$ for the highest concentration (0.02 normal) was made 100 for each value of n and the other values were proportionally varied by multiplying by the appropriate factors.

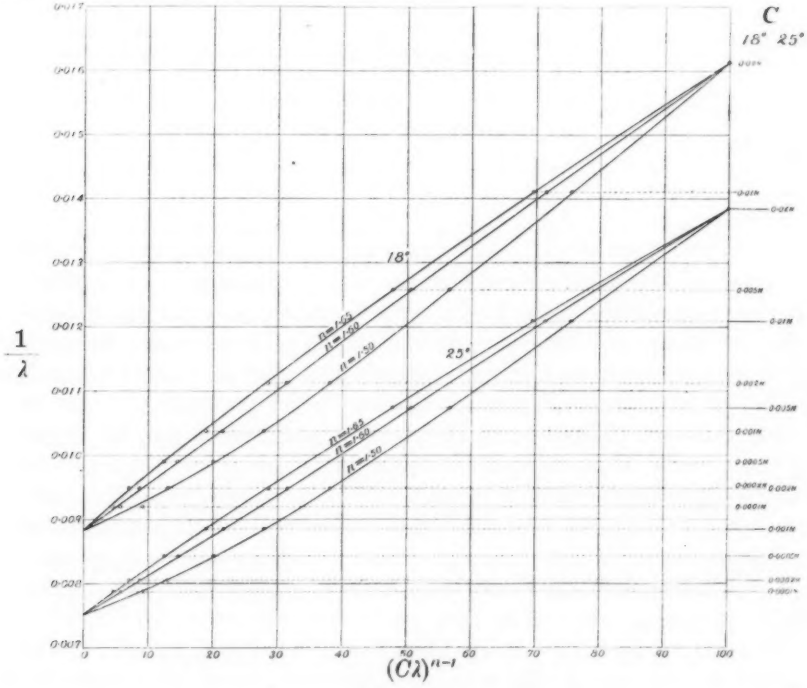

Fig. 1.

(1) Noyes and Johnston, *J. Am. Chem. Soc.*, **31** (1909), 987; Noyes and Falk, ibid. **34** (1912), 454.

It will be seen from Fig. 1, that the values of the exponent at 25° C. and 18° C. for nickel sulphate were found to be 1.6 in each case for the concentration interval from 0.0001 to 0.02 normal.

It has been found by Noyes and his co-workers that lines nearly straight were obtained with almost the same values of n for the salts of similar type, and according to Noyes and Falk (loc. cit.) for all bi-bivalent sulphates n takes a value not far from 1.6 for the concentration interval from 0.0001 to 0.02 normal. Noyes also pointed out that the variation of the exponent with the temperature is insignificant. Similar results were obtained in the case of nickel sulphate.

Table 3 contains the λ_0 values and the ionic conductances of nickel ion ($\lambda_{\frac{1}{2}Ni}$) computed therefrom and Heydweiller's values are also inserted for comparison.

TABLE 3.

Temperature.	Author.			(Heydweiller.)
	λ_0	$\lambda_{\frac{1}{2}Ni^{++}}$		$\lambda_{\frac{1}{2}Ni^{++}}$
		(I)	(II)	
18° C.	113.6	45.1	45.6	44.
25° C.	133.0	53.0	54.2	52.1

As the value of the ionic conductance of nickel changes in accordance with the value that is taken for the ionic conductance of the sulphate ion, in the calculation of the value in column (I), the necessary datum of $\lambda_{\frac{1}{2}SO_4}$ was obtained from Noyes and Falk's table (loc. cit.) and for column (II), the value of $\lambda_{\frac{1}{2}SO_4}$ in Kohlrausch-Holborn's table was used.

The Relative Viscosity and Degree of Ionization of 1/20 M. Nickel Sulphate. The measurements of relative viscosity were made with Ostwald's viscosimeter and the relative viscosity of 0.05 molal nickel sulphate at 18° C., and 25° C. was found to be 1.0209 and 1.0175, respectively.

The degrees of ionization at this concentration are obtained by using the above corresponding values of λ, λ_0 and η/η_0 at each temperature, thus:

$$\alpha \text{ at } 18^\circ\text{C.} = \frac{\lambda\eta}{\lambda_0\eta_0} = \frac{43.833 \times 1.0209}{113.6} = 0.3883$$

$$\alpha \text{ at } 25^\circ\text{C.} = \frac{\lambda\eta}{\lambda_0\eta_0} = \frac{50.75 \times 1.0175}{133.0} = 0.3939$$

Summary.

1. The conductances of aqueous solutions of nickel sulphate at concentrations 0.0001 to 1 equivalent per liter at 25° C. and 18° C. were measured and the equivalent conductances at infinite dilution were found.

2. The ionic conductances of nickel also were calculated.

3. The relative viscosity and the degree of ionization of 1/20 mol nickel sulphate were calculated.

In conclusion, the writer wishes to express his thanks to Professor G. Fuseya for his kind direction.

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THE CONSTITUENTS OF TYPHA ANGUSTATA, BORY. ET CHAUB.

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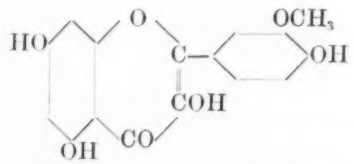
The plant, *Typha angustata, Bory. et Chaub.*, belongs to the *Typhaceae*. Its pollen has been used medicinally from remote antiquity in the East as a diuretic and a styptic. So far as I am aware, no chemical examination of this pollen appears to have been made. For the purpose of investigating its chemical constituents, it was first extracted with hot alcohol. After evaporating most of the alcohol, the residue was separated into two parts by treatment with petroleum ether.

From the soluble part in petroleum ether, a colourless substance, m.p. 62.5–63°, was obtained. The composition of this substance was $C_{16}H_{32}O_2$, and its constitution was found to be palmitic acid by analysis, molecular weight determination, and by the method of mixed melting point.

The insoluble part in petroleum ether gave a characteristic reaction to flavone by treatment with metallic magnesium and hydrochloric acid and, after being hydrolysed with sulphuric acid and then neutralised with sodium hydroxide, it reduced Fehling's solution. From these facts, this part appears to contain a glucoside of flavone. With the view to isolate the glucoside, the part was extracted with hot water, the solution precipitated with lead acetate, and the filtrate treated with basic lead acetate, by which

means a second lead precipitate was formed. The latter was decomposed with acetic acid and, after being freed from the soluble lead salt with sulphuric acid, the excess of the sulphuric acid was neutralised with barium carbonate and the barium sulphate thus precipitated was then filtered. Since the glucoside could not be obtained in a crystalline state after these treatments, it was then hydrolysed with dilute sulphuric acid, when a yellow substance (A) separated, which was collected and washed with water. From the filtrate, *d*-phenylglucosazone, m.p. 203–204°, was obtained by treatment with phenylhydrazine and acetic acid, and *p*-bromobenzoylhydrazone was also formed by the action of *p*-bromobenzoylhydrazine on it, which is soluble in a boiling mixture of alcohol, chloroform and water. These facts point to the presence of *d*-glucose in the filtrate.

The yellow substance (A) had a composition, $C_{16}H_{12}O_7$, and melted at 307°. The presence of four hydroxyl groups in the compound was proved by the formation of the tetra-acetyl derivative, $C_{16}H_8O_7(C_2H_3O)_4$, m.p. 205° and the existence of one methoxyl group, by the micro-Zeisel method. The compound, on decomposition with sodium hydroxide, gave phloroglucinol as a phenolic decomposition product and vanillic acid, as an acidic one. From these results, the constitution of substance (A) appears to be *iso*rhamnetin :



Since there was no authentic specimen of *iso*rhamnetin, the author confirmed the identity of substance (A) with it by synthesising the latter by Robinson's method,[1] and comparing their acetyl derivatives.

Experimental.

About 20 kilos. of the material were extracted by boiling with 70 % alcohol for six hours in the portion of 250 grams, 1250 c.c. of the alcohol being used for each 250 grams of the material. After the removal of most of the alcohol, the remaining alcoholic solution was shaken with petroleum ether, b.p. 50–80°, and the petroleum ether solution (a) and the alcoholic residue (b) were treated as follows :

A portion of the petroleum ether solution (a) was then mixed with acetone, when colourless crystals were deposited, which, after being recrys-

(1) *J. Chem. Soc.*, 1926, 2336.

tallised from methyl alcohol, melted at 60.5–61.5°. The filtrate was evaporated and the residual oil was distilled under a reduced pressure of 2–3 mm., when the distillate melted at 61–61.5° after recrystallisation from methyl alcohol and produced no depression of the melting point by admixture with the above specimen. After this preliminary experiment, the main portion of the petroleum ether solution (a) was evaporated and the residual oil was distilled under a diminished pressure of 2–3 mm. After recrystallising it four times from methyl alcohol, colourless crystals melting at 62.5–63° were obtained (Found: C = 74.80; H = 12.71; Mol. wt., by Rast's method, 248; 254. $C_{16}H_{32}O_2$ requires C = 74.92; H = 12.59 %. Mol. wt., 256. 3).

Titration: 0.5000 gr., dissolved in alcohol, neutralised 21.04 c.c. of an 0.0926-*N* solution of alcoholic potash, whereas this amount of a monobasic acid, $C_{16}H_{32}O_2$, should neutralise 21.07 c.c.

The identity of this acid with palmitic acid was proved by the fact that the mixture of the acid with an authentic specimen of palmitic acid caused no depression of the melting point.

After being combined with the alcoholic residue (b) from several separate experiments, it was further concentrated to 4 litres under diminished pressure, diluted with 24 litres of water and heated on a water-bath for 2.5 to 3 hours. The light, brown, aqueous solution thus obtained was again evaporated to one-fourth of its bulk.

(1) **The Determination of Reducing Sugar combined with Flavone.** The glucoside of flavone was precipitated by basic lead acetate, the precipitate was decomposed with dilute acetic acid (50 %) and freed from the soluble lead compound with sulphuric acid. The excess of sulphuric acid was then neutralised with barium carbonate, and the barium sulphate thus precipitated was filtered. As the glucoside of flavone was difficult to obtain in a crystalline state, sulphuric acid was added till the solution contained 4 per cent of this acid and heated on a water-bath, when a yellow substance (A) was obtained, which was collected and washed well with water. The yield was 50 grams. A portion of the filtrate was warmed with phenylhydrazine and glacial acetic acid, when brownish yellow crystals separated. After being recrystallised from alcohol, the crystals melted at 203–204° and caused no depression of the melting point by admixture with *d*-phenylglucosazone. In order to decide whether the reducing sugar is glucose or mannose, another portion of the filtrate was treated with acetic acid and *p*-bromobenzoylhydrazine, when colourless crystals were obtained, which were clearly dissolved in a boiling mixture of alcohol, water and chloroform. It thus follows that the reducing sugar is *d*-glucose.

(2) **The Determination of Yellow Substance (A).** After being recrystallised from methyl alcohol, it separated in lemon-yellow crystals, m.p. 307° (decomp.) (Found: C = 60.61; H = 3.99; CH_3O, by the micro-Zeisel method = 9.58; Mol. wt., by the Rast method, 303. $C_{16}H_{12}O_7$ requires C = 60.74; H = 3.80; CH_3O = 9.80 %. Mol. wt., 316).

The Acetyl Derivative. This compound was prepared by heating the substance with acetic anhydride and fused sodium acetate, and melted at 204–205° (Found: C=59.59; H=4.28. $C_{24}H_{20}O_{11}$ requires C=59.51; H=4.13 %).

The Decomposition of Yellow Substance (A) with Sodium Hydroxide. The substance (1 gram) was dissolved in a solution of 2 grams of sodium hydroxide in 12 c.c. of water and a current of air was passed through it for three hours, when the colour of the solution turned a brownish yellow. The solution was neutralised with sulphuric acid, and, after an excess of sodium bicarbonate had been added, it was extracted with ether. The ethereal solution (c) and the aqueous residue (d) were treated in the following way:

(c) After the removal of the ether, the residue was recrystallised from water with the addition of animal charcoal, when colourless crystals were obtained, which, drying at 105–110°, melted at 216–217°. This substance did not depress the melting point after being mixed with anhydrous phloroglucinol, being undoubtedly identical with the latter.

(d) The aqueous residue was acidified with hydrochloric acid and extracted with ether. After evaporating the ether from the ethereal solution, the residue was recrystallised from water with the addition of animal charcoal. The substance thus purified melted at 206–207° and its melting point was not depressed by admixture with an authentic specimen of vanillic acid.

Synthesis of *iso*Rhamnetin. In order to prove the identity of yellow substance (A) with *iso*rhamnetin, the latter was synthesised by Robinson's method.

For this purpose, vanillic acid was first synthesised by a modification of the method described in the report on the German patent No. 258887. *iso*Rhamnetin was then synthesised from vanillic acid by following exactly the directions given by Robinson and converted into the tetra-acetyl derivative, m.p. 204–205.5°. The melting point of this substance was not depressed by admixture with the acetyl derivative of yellow substance (A), thus leaving no doubt as to identity of yellow substance (A) with *iso*rhamnetin.

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